SUMMARY

Hindered internal rotation and long-range shielding in alkyl N-[(arylsulfonyl)methyl]carbamates:

$$RSO_2CH_2\underset{\underset{R'}{|}}{N}CO_2R''$$

(R = aryl, R' = H, alkyl, R'' = alkyl)

have been the subjects of our investigation.

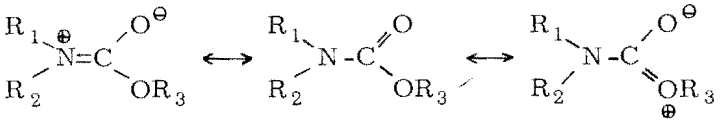
After a few introductory remarks, the various NMR methods for studying exchange reactions are discussed, together with known synthetic methods for preparing the carbamates (chapter I).

The synthesis of some of the compounds studied is described in chapter II.

A discussion of the high resolution NMR method for studying line shapes of exchange reactions is given in chapter III. Throughout the literature many studies using this method have been published. In most of these, single parameter approximations of the complex semi-classical equation, describing exchange broadened line shapes, have been employed. A short survey of these approximate techniques is given. Recently the single parameter methods have been criticized since they are often liable to large systematic errors in the kinetic parameters obtained. Therefore, we have developed a procedure in which the semi-classical equation is used without approximations. A total line shape technique is applied in which the rate constants of the exchange reaction are extracted from the broadened NMR curves by an iterative computer programme.

The kinetic parameters of hindered internal rotation around the nitrogen to carbonyl carbon bond have been determined for several alkyl N-methyl-N-[(arylsulfonyl)methyl]carbamates and for methyl N-methyl-N-[(p-tolylthio)methyl]carbamate (chapter IV). The values obtained for the activation energy are lower than those for amides. This is, to a first approximation, in accordance with the theory of cross-conjugation which states that the bond order of the amide bond

in carbamates should be lower than in amides. Electron delocalization from the ether oxygen atom into the carbonyl function competes with that from the nitrogen atom.



As we have not carried out an extensive study of possible medium effects on the rotation barrier, a comparison with amides is rather difficult.

Systematic errors may also occur when a total line shape method is used, for in our method the choice of the input line width values, required in the computer processing, has been found to be critical. Errors of this kind can only be avoided when: a. distinctly exchange broadened NMR curves are used. b. systems are used in which the chemical shift between the signals of the exchanging nuclei is large compared with the non-exchange line widths.

The NMR absorptions of the ester groups of alkyl N-[(arylsulfonyl)methyl]carbamates are doublets of unequal intensity at temperatures where rotation around the amide bond is very slow. At least one of the signals shows an appreciable upfield shift when compared to simple carbamates. The shift is proportional to the ring current in the aromatic nucleus of the molecule. This is explained by assuming the existence of favourable conformations, having the aromatic ring situated near the ester group (chapter V). Evidence for such conformations is obtained by comparing NMR spectra of a large number of related structures. A study of solvents effects on, and temperature dependence of, chemical shifts lends further support to this hypothesis. Chemical shift data for some thiol-, thion- and dithiocarbamates are also compared.

The computer programme (written in Algol) and a short discussion is given in the Appendix.